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On a correlation between electronic charge density overlap and Born-Mayer parameters of alkali halides

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Empirical correlations between Born-Mayer repulsive parameters of alkali halides and overlap parameters of free ion electronic charge-densities have been obtained. The correlations are found satisfactory for chlorides and bromides though flourides show some deviations.

1. Introduction

At present, the repulsive interaction between ions in an ionic lattice is usually taken in the form (Tosi 1964)

$$E_{ij}^{rep}(r) = \beta_{ij} b \exp((r_i + r_j - r)/\rho), \qquad \ldots (1)$$

where b and ρ are repulsive *strength* and *range* parameters respectively, r_i and r_j are ionic radii and β_{ij}, termed the Pauling coefficient, is defined as

$$\beta_{ij} = 1 + Z_i/n_i + Z_j/n_j. \qquad \ldots (2)$$

In eq. (2) Z_i, Z_j are valence of the interacting ions while n_i, n_j are numbers of electrons in the outermost shells of these ions. For the nearest neighbours interaction, $\beta_{ij} = 1$ for all alkali halides excepting the lithium halides.

Repulsive strength and range parameters, b and ρ respectively, are usually found out by utilizing equilibrium crystal properties, namely,

(i) equilibrium condition,

$$\left.\frac{dU(r)}{dr}\right|_{r=r_0} = 0 \qquad \ldots (3)$$

and (ii) compressibility at absolute zero, K_0,

$$\left.\frac{d^2U(r)}{dV^2}\right|_{V=V_0} = \frac{1}{-v_0 \cdot 0} \qquad (4)$$

where $U(r)$ is the interionic potential, r_0 is the equilibrium interionic separation, V_0 is the volume of the crystal corresponding to an equilibrium separation r_0; V corresponds to the variable r.

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b and ρ, thus found out from perfect crystal properties, construct the repulsive part of a potential which reproduces successfully many of the properties of a perfect ionic crystal. Even many defect properties, for example, Schottky and Frenkel defect formation and migration energies, enthalpy of formation and migration of a homovalent impurity etc., can be predicted in a satisfactory way with the help of these b and ρ. However, the situation becomes a little different when a neutral atom or an aliovalent impurity is substituted in a lattice site. Then, one has to recourse to approximations, over and above the normal approximations which are made in these calculations, regarding the nature of interaction between the impurity and the surrounding ions. Quite often one may find out a suitable device, such as the thermochemical cycle, through which revised parameters of interaction of the impurity ion in a new neighbourhood can be figured out (Bowman 1971), while there are other situations, too, where no such method is available, for example the inclusion of inert gas atoms in an ionic lattice, and one has to depend entirely on educated guesses and ultimately judge them from the final result.

Perhaps, the origin of this state of affairs is that no physical basis has been ascribed to the Born-Mayer parameters. In other words, these are just numbers associated with the repulsive interaction of a particular ion-pair and we know how to figure them out from crystal properties but we have not tried to associate them to properties of the ions themselves. If that could be done, that is, if b and ρ could be derived from properties of the interacting ions, one would not need to make any guesswork.

In this note, we present an empirical way of finding out Born-Mayer parameters from free-ion charge desities and equilibrium interionic separation of the alkali halides. Over and above its simplicity, this method has the advantage that b and ρ have been correlated to some reasonable physical quantities and therefore are not arbitrary constants. Consequently, the method has the potentiality of being extended to the question of finding out parameters for any impurity in an alkali halide host lattice. We present below our observations and the correlations.

2. Correlations and Discussions

If electronic charge densities of the interacting ions are plotted in the manner shown in figure 1, it is found

(i) that a particular alkali ion has a fixed overlap height, h, for Cl^- and Br^- ions and a slightly different h for F^- ions;

(ii) the spread of overlap, s, has a linear relation with the range parameter, ρ, as can be seen from figure 2;

(iii) $\ln(h^2 r_0^5)$ vs. $\ln(\beta_{ij} b)$ plot seems to be linear too (figure 3); it may be noted that $h^2 r_0^5$ has the same dimension as $\beta_{ij} b$.

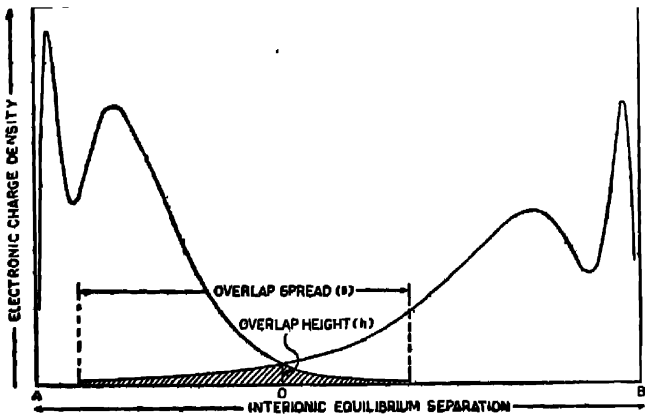

Fig. 1. Schematic of the plot for estimating overlap parameters, s and h. A, B—positions of centres of ions.

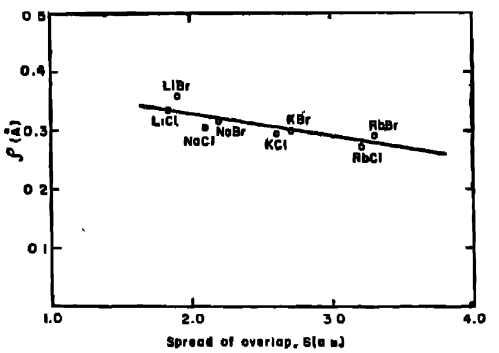

Fig. 2. ρ vs. s plot for chlorides and bromides. Continuous line is obtained from a least squares fit of the points to a linear relation between ρ and s (eq. (6)).

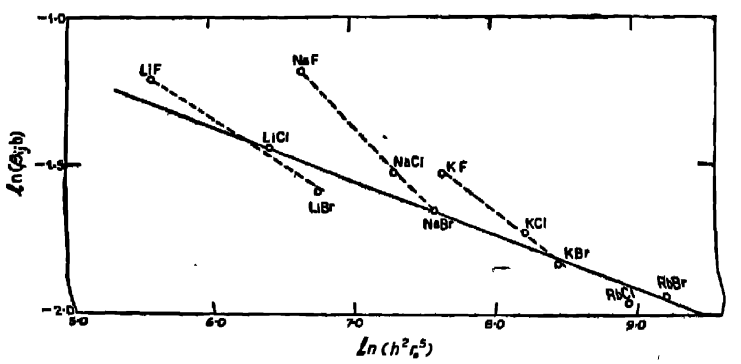

Fig. 3. $\ln(\beta_{ij}b)$ vs. $\ln(h^2r_0^5)$ plot for different crystals. Continuous line has been obtained from a least squares fit of the points to a linear relation between $\ln(\beta_{ij}b)$ and $\ln(h^2r_0^5)$ (eq. (5)).

In these plots, we have used b, ρ, and r_0 data of Chaudhuri *et al* (1974), which have been determined from extrapolated 0°K values of the most recent elastic constant and density measurements of alkali halides. Electronic charge densities (normalized) are either taken from different calculations of Hartree & Hartree (1935, 1936, 1938, 1948) or are derived from the Clementi (1965) wavefunctions. Hartree and Clementi values agree well among themselves. We could not include iodides because of the non-availability of state-functions of I^-. Flourides have also been excluded because of their derivation from this general picture. At present, we can not ascertain whether their large Cauchy violations (Born & Huang 1954), or a possible large modification of the free-ionic charge density in a crystalline configuration, is responsible for this behaviour.

Correlations thus obtained can be written as :

$$\ln(\beta_{ij}b) = -0.2246 - 0.187 \ln(h^2 r_0^5), \quad \ldots (5)$$

and

$$\rho = 0.41/0.0406. \quad \ldots (6)$$

In eqs. (5) and (6), h, r_0 and s are to be substituted in atomic units to get β_{ij} b in 10^{12} dyne cm and ρ in Å. s in eq. (6) has to be figured out from the overlap spread at 0.01 atomic unit of charge density. Alternatively, it could be found out from the spread at any other reasonable charge density but the constant in eq. (6) would then change, the slope remaining almost constant. This follows from the geometry of the region of overlap. In table 1 we have recorded b, ρ and s values for chlorides and bromides.

Table 1. Equilibrium interionic separation, and overlap and Born-Mayer parameters for different crystals.

Crystal	$b(10^{12}$ dyne cm)	ρ(Å)	r_0(Å)	h(a.u.)	s(a.u.)
LiCl	0.235	0.333	4.795	0.50	1.83
LiBr	0.203	0.361	5.126	0.50	1.90
NaCl	0.216	0.306	5.271	0.61	3.10
NaBr	0.190	0.316	5.575	0.61	3.20
KCl	0.177	0.294	5.872	0.74	2.61
KBr	0.159	0.300	6.155	0.74	2.71
RbCl	0.141	0.272	6.119	0.94	3.21
RbBr	0.143	0.292	6.439	0.94	3.31

We have made a few other observations which are given below

(i) If ions are thought to *touch* at the equilibrium separation, corresponding ion size (AO and BO in figure 1) are very nearly equal to Pauling radii. The variation of alkali ion sizes, measured in this way, is small while that of halogen ion size is perceptible.

(ii) In $\ln(\beta_{ij}b)$ vs. $\ln(h^2r_0^5)$ plots, Li, Na and K- halides, with the exception of Rb-halides, form different straight lines. This has been indicated by dashed lines in figure 3. In these lines, flourides can also be included.

(iii) It seems, reasonable $\beta_{ij}b$ and ρ values may be obtained for a Ca^{++} impurity ion (the electronic charge density of which is available) in an alkali halide lattice.

However, these observations are still in an incomplete state and we would like to process them a little more and present them in a future communication.

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